

## PHENOLIC -OH AS A PROCESS-PERFORMANCE INDICATOR IN TWO-STAGE LIQUEFACTION

G. A. Robbins, R. A. Winschel and F. P. Burke

CONOCO INC.  
Coal Research Division  
4000 Brownsville Road  
Library, PA 15129

### ABSTRACT

Phenolic -OH concentrations were measured for process oil samples taken throughout the year-long Run 3LCF9 of the Lummus Integrated Two-Stage Liquefaction PDU, and a 25-day run of HRI's bench scale Catalytic Two-Stage Liquefaction process unit. The phenolic -OH concentration of the Lummus product resid responded to changes in catalyst age and space velocity. The phenolic -OH concentration of the HRI second-stage products also increased in response to catalyst age, the only process variable during that run. These results demonstrate that phenolic concentration is a sensitive indicator of coal liquefaction process performance. These data were obtained using a quantitative infrared spectroscopic method, applicable to tetrahydrofuran-soluble coal liquids, which permits analysis of the entire range of converted coal products. This analytical method is rapid, reproducible and accurate, and also provides qualitative information about the molecular structure of the phenolic components.

### INTRODUCTION

The successful operation of a coal liquefaction process requires some means to monitor process performance as a function of time and changes in operating conditions. Operating history and material balance data are essential, but require substantial time for analysis, calculations and compilation. Alternatively, selective chemical characterization techniques can provide a great deal of process performance information within minutes after samples are obtained. A principal objective of our coal liquefaction research has been to develop rapid reproducible analytical methods for coal liquids characterization and process monitoring.

Extensive application of these techniques has shown that the phenolic OH concentrations of coal liquids are very useful in monitoring process performance. These data give evidence of approach to or achievement of steady-state operation. They provide information on the extent of deoxygenation, which can be used to assess catalyst deactivation in a process such as two-stage liquefaction. Changes in phenol concentration can also result from changes in operating conditions. Phenolic OH concentrations supplement other data to provide a broad picture of process performance and product characteristics.

This paper presents two applications of an infrared spectroscopic method for phenolic OH.

### RESULTS AND DISCUSSION

#### Summary of Infrared Method

In this method, the phenol concentration is determined from the height of the peak in the infrared spectrum produced by the stretching vibration of the phenolic O-H bond in dilute tetrahydrofuran (THF) solution (Figure 1). The infrared spectra were obtained using a Nicolet Model 7199C Fourier transform infrared (FTIR)

instrument operated at a nominal resolution of  $4\text{ cm}^{-1}$  (data were collected every  $2\text{ cm}^{-1}$ ).

A software peak-picking routine was used to locate the maximum in the phenolic OH stretch band found around  $3300\text{ cm}^{-1}$ . The baseline value used was the average absorbance over  $3750\text{--}3650\text{ cm}^{-1}$ . The net absorbance used for quantitation was the OH stretch peak absorbance minus the baseline absorbance. Measurements were limited to the  $0.3\text{--}1.0$  net absorbance range. A linear least-squares fit of absorbance vs (concentration  $\times$  path length) for standard solutions provided the calibration (extinction coefficient) for phenols determination in actual samples. A detailed description of this method and its verification by an independent  $^{19}\text{F}$ -NMR technique have been reported (1).

Other methods for the determination of phenols in coal liquids (using nuclear magnetic resonance (NMR) spectrometry or infrared (IR) spectroscopy) have typically employed chloroform or methylene chloride as solvents for analysis. However, because THF is a much better solvent than these for dissolving coal liquids, almost the entire sample from any liquid process stream becomes available to the analysis method, particularly if "THF solubles" is used to define converted coal products. A significant advantage of the IR technique is that minimal sample preparation is required. In addition, because the instrument produces digitized data, the peak location and background and peak absorbances are determined automatically, greatly facilitating the analysis. Using this method, we can routinely complete 3-4 phenolic -OH determinations per hour, including sample preparation and clean-up.

Possible common interferences to determination of phenolic OH content by this method are water and amine groups (particularly pyrroles). Water in moderate amounts poses no particular problem, and the question of interferences by amines remains to be resolved and is an active area of our investigation.

Based on the model compound data, phenol concentrations are accurate to  $\pm 0.1$  meq OH/g sample (95% confidence) over the range of concentrations typical for coal liquids. Reproducibility for resid samples was  $\pm 0.09$  meq OH/g sample for concentration and  $\pm 1\text{ cm}^{-1}$  for frequency.

Consistent calibration data for quantitative analysis were obtained from a wide range of model compound phenols (Figure 2). This is necessary for accurate quantitation. The frequencies of the peaks varied somewhat from one model phenol to another, demonstrating a trend with ring condensation and with phenol aqueous acidity (Figure 3). The frequency observed for a particular phenol depends on the O-H bond strength, which is related to the chemical structure and is reflected in the acidity (as the aqueous dissociation constant). A low frequency results from a weaker O-H bond (more acidic) as in the multiple-ring phenols. Ring condensation withdraws electrons, thus weakening the O-H bond. Conversely, alkyl substituents donate electrons, producing a stronger O-H bond, lower acidity, and higher infrared frequency. Thus, the infrared frequency of the OH peak is roughly related to ring condensation and alkyl substitution. The model compound data indicate a single- vs multiple-ring frequency cutoff in the  $3275\text{--}3300\text{ cm}^{-1}$  region. Because of these observations, we explored the potential utility of the frequency data to provide qualitative information on process samples. These results are discussed below.

#### Lummus ITSL Run 3LCF9 Process Description and Run Summary

Run 3LCF9 was a year-long run of the Integrated Two-Stage Liquefaction (ITSL) process at Lummus' 30 lb/h PDU. The three major process units are: 1) plug flow, short contact time, first stage (SCT unit) operated at  $830\text{--}865^\circ\text{F}$ , 2 to 10 min, and  $2000\text{--}2400$  psig, 2) an interstage antisolvent deashing unit (ASDA), and

3) an expanded-bed catalytic hydrotreater second-stage (LC-Finer), operated at 720-750°F, 2700 psig, and 0.6 - 1.8 lbs feed/lb cat h. These three sub-units serve distinct functions. The SCT unit dissolves the coal (~92% MAF), the ASDA removes solids, and the LC-Finer converts resid to lighter products, prepares a suitable donor solvent and removes heteroatoms from the net product.

Run 3LCF9 was made with clean Burning Star (Illinois 6) coal and a single charge of fresh Shell 324M (Ni/Mo) catalyst. Major variables during the run were catalyst age, space velocity, temperature, and feed source.

During the first third of Run 3LCF9, the PDU was operated as described above. During the middle of the run the order of the ASDA and LC-Finer was inverted, i.e., the LC-Finer processed ash-containing feed and the LC-Finer product was deshed. Later in the run, the ASDA and LC-Finer were returned to their original order and a partially back-mixed soaker reactor was added to the SCT unit. The soaker was operated at a lower temperature (830°F) and pressure (1000-2000 psig) but longer residence time (10-15 min) than the SCT coil-only reactor.

The discussion below describes characterization of the second-stage (LC-Finer) operations in terms of the -OH concentrations of the THF-soluble 850°F<sup>+</sup> feeds and products. A detailed description of Run 3LCF9 (4, 5, 6) and thorough analytical characterization results (1, 7) have been reported.

#### Phenol Concentration Response

Figure 4 plots the change in phenolic concentration (feed minus product) for the soluble resid samples of ITSL Run 3LCF9 as a function of catalyst age: the greater the value, the greater the reduction in phenolic functionality in the LC-Finer system. Phenolic concentrations ranged from 1.1 to 1.6 meq/g for the feed resids and from 0.4 to 1.6 meq/g for the product resids.

The general decrease in phenolic removal with catalyst age at constant space velocity is apparent. It is also evident during the parts of the run operated with all variables held constant, such as those at 750°F (early in the run) and at 780°F. This represents deactivation of the catalyst's deoxygenation activity.

The data around 600 and 1800 lb 850°F<sup>+</sup>/lb cat show the clear effect of space velocity. Operation of the process at lower space velocity increased phenol removal by decreasing the phenolic OH concentration in the products. Conversely, operation at higher space velocity decreased phenol removal by increasing the phenol content in the products. Although temperature and feed source were also variables during Run 3LCF9, the phenol concentrations in the products showed no obvious response to these changes. Thus, the phenol concentrations of Run 3LCF9 products were sensitive to catalyst age and space velocity, but not to the other variables.

In addition to showing response to certain planned process variables, phenolic OH concentration is also sensitive to unplanned changes in conditions, as the following example shows. Three points between catalyst age 400-500 lb 850°F<sup>+</sup>/lb cat show anomalously low phenol removals (Figure 4). For these three run periods, the product samples had unusually high phenolic concentrations. These three were the earliest samples we received following a departure from planned operating conditions which was reported by Lummus (4, 5). If frequent sampling and analysis were performed on a continuing basis during plant operations, such deviations from desired conditions might be recognized and corrected earlier.

### Phenol Frequency Response

The phenol peak frequency was sensitive to catalyst age, but not to the other variables (Figure 5). These data show much less variation than the concentration data. The product resid peaks consistently occur at higher frequency than the feed resid peaks (product 3289-3306  $\text{cm}^{-1}$  vs feed 3282-3288  $\text{cm}^{-1}$ ), in agreement with the structural interpretation of the model compound frequency data. The upgraded product resids have a lower degree of ring condensation than the feed resids, hence the higher frequency of the product resid peaks. For the same reason, the distillate phenol peaks occur at higher frequencies than the peaks from the corresponding resids. In the present application, the decrease of the product resid peak frequency with increasing catalyst age is an indication of catalyst deactivation. Both the concentration and frequency data indicate that two stages of catalyst deactivation may be present. A very rapid deactivation for the initial part of the run is followed by a more gradual one for the remainder of the run.

### CTSL Run 227-20 Process Description and Run Summary

HRI's catalytic two-stage liquefaction (CTSL) process consists of two catalytic ebullated-bed reactor stages for coal hydrogenation and liquefaction. In the first stage, a coal slurry prepared from process-derived heavy recycle oil is treated with hydrogen at temperatures below 800°F. These conditions are designed to hydrogenate the coal matrix while maintaining the solvent donor quality. The low temperature minimizes dehydrogenation, cracking, polymerization, and condensation reactions. The first-stage products pass directly to the second stage, where higher temperature hydrotreatment, liquefaction, and heteroatom removal take place. Atmospheric still bottoms, vacuum still overheads, and pressure filter liquid (PFL) from the atmospheric still bottoms are combined to make the recycle oil. A summary of CTSL development has been reported (8).

Run 227-20 was conducted as a bench-scale demonstration of CTSL technology. Burning Star (Illinois 6) coal was processed at constant conditions for 22 days after a three-day startup period. Operating conditions reported by HRI (8) are given below:

#### OPERATING CONDITIONS HRI CTSL Run 227-20

Feed: Illinois No. 6 Coal, Burning Star Mine, -70 US mesh,  
2.5/1 Solvent/Coal  
Catalyst: First Stage - Amocat 1C (Ni/Mo)  
Second Stage - Amocat 1A (Co/Mo)  
First Stage Temperature - 750°F  
Second Stage Temperature - 825°F  
Unit Back Pressure - 2500 psig  
Dry Coal Space Velocity (each Stage), lb Dry Coal/h/ft<sup>3</sup> cat - 68

Conoco received daily PFL samples from the run and performed analyses on selected samples. The PFL represents the solids-free portion of the major second-stage product, which is recycled to the first stage. The complete characterization data have been reported (1).

### Phenol Concentration Response

Phenolic OH concentrations of 850°F<sup>-</sup> distillate and THF-soluble 850°F<sup>+</sup> resid samples from Run 227-20 are plotted in Figure 6 as a function of run day. There

is an initial reduction in distillate and resid phenolic OH content during the three day startup period, as the startup solvent was replaced by coal liquids low in phenols, produced over the fresh catalyst. From day 4 to day 25, as the catalyst aged, the phenol concentrations of the PFL distillates and resids increased as shown in Figure 6.

The observation that these samples became more phenolic with time is consistent with HRI's process performance data which also show a decrease in catalyst activity with time (see below).

#### CTSL RUN 227-20 PROCESS PERFORMANCE DATA (Reference 8)

Period	5	10	15	19	24
Avg Cat Age,					
lb Dry Coal/lb Cat	216.3	441.3	664.3	844.2	1069.1
975°F Conversion, wt % MAF	86.9	83.6	82.2	80.6	77.2
C <sub>6</sub> - 975°F, wt % MAF	72.3	68.0	67.2	65.4	62.6
Organic Sulfur Removal, wt %	98.0		96.6		94.6
Nitrogen Removal, wt %	79.2		66.5		56.4

The increase in phenolic concentration represents deactivation of the catalyst's deoxygenation activity. The deactivation exhibited by the distillate phenol data is highly linear with catalyst age and showed no evidence of subsidence at the end of the run.

The increase in phenolic content of the 850°F<sup>+</sup> resid samples was not linear (Figure 6). There was a rapid increase in phenolic content up to about day 12 followed by a more gradual increase. This may indicate that the catalysts' initial activity for removal of phenols from the resid was substantially lost by day 12. One would expect the resid molecules to be excluded from the active catalyst sites by pore mouth blockage before the distillate molecules would be excluded. The observed difference between the distillate and resid phenolic OH concentration response with time suggests that the distillate and resid fractions have different rates and/or mechanisms of deactivation toward deoxygenation.

#### Phenol Frequency Response

The phenol infrared peak frequency data from the distillate and resid samples are plotted in Figure 7 as a function of run day. The distillate peaks were consistently observed at higher frequency than the resid peaks. This fits the structural model for these data, with the distillates containing phenols of smaller ring size than the resids. These frequencies decrease throughout the run, consistent with a continual catalyst deactivation. In contrast to the concentration data, the frequency data do not show a trend reversal after startup. The reason for this is not clear, but the result implies that the concentration and frequency data are independent measurements, even through a high peak frequency and low phenol concentration tend to correlate. It is probable that the two concentration and frequency trends during startup reflect differences in the molecular composition of the startup and process oils, and that inventory replacement was complete by day 4, as the concentration data indicate.

The distillate and resid frequency appear to follow curves of nearly identical shapes, in contrast to the concentration data. The interpretation of the frequency data is not completely straightforward, but future application of the data may suggest a more meaningful interpretation of the results.

## CONCLUSIONS

Phenolic OH concentration can be a useful indicator of coal liquefaction process performance. Such data are sensitive to process variables such as catalyst age and space velocity, and to changes during startup and process upsets. The infrared spectroscopic method employed permits useful data to be obtained from residual oils, for which few analytical methods are available. Data from CTSL Run 227-20 suggest that distillate and residual oils may have different rates and/or mechanisms for deactivation of the catalyst toward deoxygenation reactions.

Use of the infrared frequency data provided by the method may give qualitative information about the molecular structure of phenols present in each sample. Interpretation of these data may not be straightforward, but might be improved after broader application.

Continued application of this method to liquefaction process monitoring should lead to a clearer picture of changes during specific process runs, and should aid in a general understanding of liquefaction chemistry, particularly in the heavier materials.

## ACKNOWLEDGEMENT

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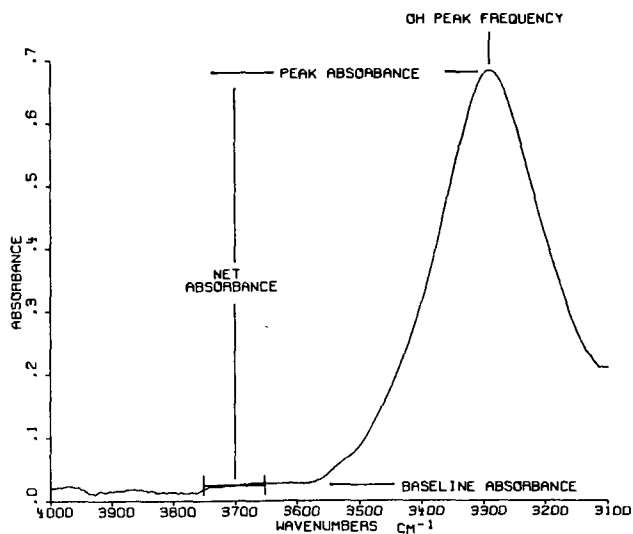


Figure 1. Infrared Spectrum of a Distillate Sample in THF.

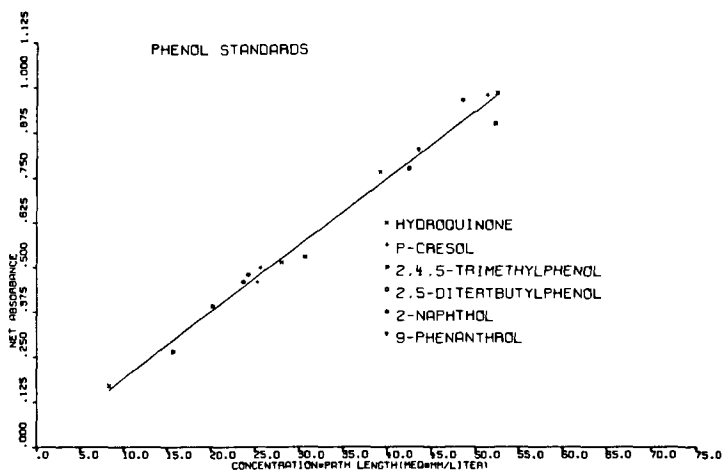
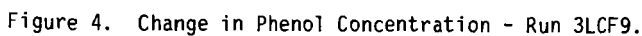
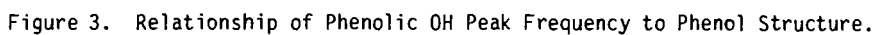


Figure 2. Model Compound Phenol Calibration Data and Least-Squares Line.





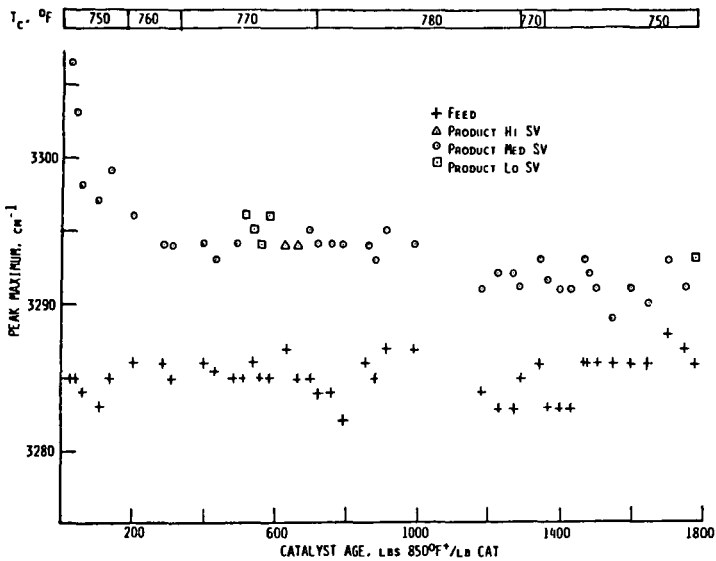


Figure 5. Frequency of Phenol Peak Maximum - Run 3LCF9.

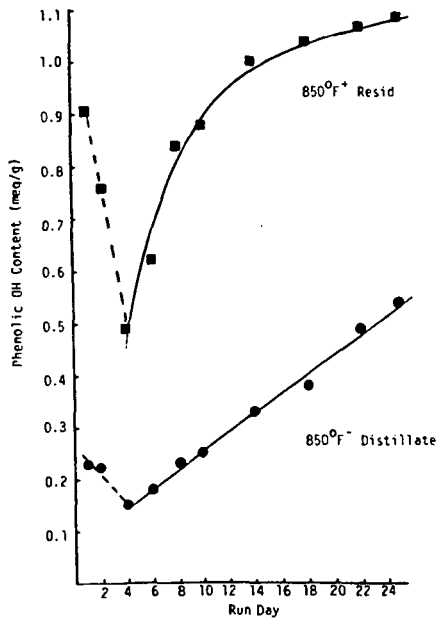


Figure 6. Phenolic OH Content vs Run Day - Run 227-20.

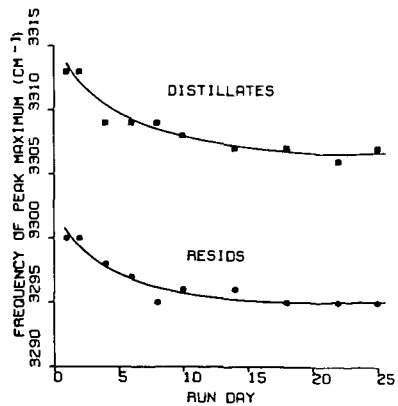


Figure 7. Phenol Peak Frequency vs Run Day - Run 227-20.